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TI Manufacture of copper-titanium alloy sheets having improved bending and stress relaxation property

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AB Cu alloys containing 0.01-4.0% Ti are solution treated at ≥800° for <240 s under control of average grain size at ≤20 μm, cold rolled with <80% draft, solution treated at ≥800° for <240 s under control of average grain size at < 1-20 μm, cold rolled with ≤50% draft, and aged at 300-700° for ≥1 h but <15 h to obtain the title sheets. Optionally, the Cu-Ti alloy contains addnl. 0.05-2.0% Zn and 0.01-3.0% Cr, Zr, Fe, Ni, Sn, In, Mn, P, and/or Si.

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Notes:

1. Untranslatable words are replaced with asterisks (****).

2. Texts in the figures are not translated and shown as it is.

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FULL CONTENTS

[Claim(s)]

[Claim 1] [contain Ti:0.01-4.0% at a weight rate, and / the remainder / the copper alloy which consists of Cu and an unescapable impurity] (1) The 1st solution treatment performed by the heat treatment condition in which less than 240 seconds and an average crystal grain diameter do not exceed 20 micrometers at the temperature of 800 or more degrees C, (2) The 1st cold rolling performed with less than 80% of workability, the 2nd solution treatment performed by the heat treatment condition used as the range in which less than 240 seconds and an average crystal grain diameter do not exceed 1-20 micrometers at the temperature beyond (3) 800 degree C, (4) The manufacture method of a titanium copper alloy excellent in the bendability and the stress relaxation characteristic which are characterized by performing aging treatment of less than 15 hours one by one for 1 hour or more at the 2nd cold rolling performed with 50% or less of workability, and (5)300-700 degree C temperature.

[Claim 2] Contain Ti:0.01-4.0% at a weight rate, and 0.01 to 3.0% is further contained for one or more sorts of Zn:0.05-2.0% and Cr, Zr, Fe, nickel, Sn and In, Mn, and P and Si in a total amount. The 1st solution treatment performed by the heat treatment condition to which less than 240 seconds and an average crystal grain diameter do not exceed 20 micrometers at the temperature beyond (1) 800 degree C to the copper alloy with which the remainder consists of Cu and an unescapable impurity, (2) The 1st cold rolling performed with less than 80% of workability, the 2nd solution treatment performed by the heat treatment condition used as the range in which less than 240 seconds and an average crystal grain diameter do not exceed 1-20 micrometers at the temperature beyond (3) 800 degree C, (4) The manufacture method of a titanium copper alloy excellent in the bendability and the stress relaxation characteristic which are characterized by performing aging treatment of less than 15

hours one by one for 1 hour or more at the 2nd cold rolling performed with 50% or less of workability, and (5)300-700 degree C temperature.

[Detailed Description of the Invention] [0001]

[Industrial Application] This invention relates to the manufacture method of a titanium copper alloy excellent in bendability and a stress relaxation characteristic. If it states in more detail, it is related with the manufacture method of the titanium copper alloy used for manufacture of the product of all fields with which good bendability including electronic parts, such as various terminals, a connector, a relay, or a switch, is required, and high spring nature is demanded.

[0002]

[Description of the Prior Art] In the ingredient which needs the electrical conductivity and spring nature of the various terminals of an electrical and electric equipment, a connector, a relay, or a switch, it is a former and cost side. Nickel silver was applied for the application than to which inexpensive "brass" is applied for the application to think as important, and phosphor bronze is applied for the application than to which greater importance is attached to spring characteristics, or greater importance is attached to spring characteristics and corrosion resistance.

[0003] However, since it cannot say in recent years that these ingredients can not necessarily satisfy hardness in connection with electrical and electric equipments, and a miniaturization and thinning inclination of the component, it is, The need of the high-class spring material which has high intensity, such as beryllium copper (a "Cu-Be alloy" is called below) and titanium copper (a "Cu-Ti alloy" is called below), is increasing.

[0004] JP,H2-49379,B Ti:0.1-3.0%, Si:0.03-1.5%, [the rate of a Ti/Si bulk density / the Cu-Ti alloy which has the presentation of 2-4 and carried out the distributed deposit of the Ti-Si system intermetallic compound into Cu matrix] Tension annealing which improves hot-rolling of a cast piece (ingot), the full dissolution of Ti and Si by quenching from hot-rolling finishing temperature, cold rolling, annealing that deposits a Ti-Si system intermetallic compound, ductility, and bending nature is performed one by one. It is manufacturing.

[Problem(s) to be Solved by the Invention] Since small and light-ization of electrical and electric equipments and the component of those is progressing increasingly in recent years, the claim to the hardness and bendability of an ingredient is severe. With the Cu-Be alloy, in order to cater to the claim of such severe bending, the method of performing strong bending in the state of solution treatment, heat-treating after that, and obtaining hardness is enforced, but by this method, the electronic-parts manufacturer side who uses an ingredient must perform a heat treatment process.

Therefore, the claim is increasing so that the ingredient which does not need to be a heat treatment

process may be offered after bending as an electronic-parts manufacturer side, and it is expected with the further future formation of components small and light that this claim increases further. Moreover, although the Cu-Be alloy has high hardness, since there is toxicity strong against beryllium and a special manufacturing facility is needed, it has the defect that a price is expensive. [0006] The tensile strength of the Cu-Ti-Si alloy proposed by above-shown JP,H2-49379,B is about 54-61kg/mm2. It is and electric conductivity is about 37 to 50%IACS. (Chip box) Although the good result had been obtained about bendability, it was not obtained with the ingredient which is equal to a Cu-Be alloy.

[0007] Then, in order that this invention person etc. may improve the bendability and hardness of a Cu-Ti alloy, As a result of repeating investigation wholeheartedly paying attention to the number of times of the crystal grain diameter and cold rolling, and solution treatment, it became clear by adjusting the average crystal grain diameter of a Cu-Ti alloy to 1-20 micrometers that hardness and bendability are improved. That is, this invention offers the manufacture method of a high strength copper alloy of having improved the bendability and hardness of a Cu-Ti alloy.

[Means for Solving the Problem] The result of having repeated investigation wholeheartedly paying attention to the number of times of a crystal grain diameter and cold rolling, and solution treatment so that this invention person etc. may improve the bendability and hardness of a Cu-Ti alloy, As an alloy content At a restricted specific rate, strictly [Ti] In advance of; 2 times cold rolling made to contain, [solution treatment]; performed for every time --; made into the conditions which adjust the average crystal grain diameter of Cu crystal which makes Ti after the treatment concerned solute for the 1st solution treatment to 20 micrometers or less --; which adjusts the average crystal grain diameter by the 2nd solution treatment to 1-20 micrometers in the state of a particle size regulation -- [preventing big and rough-ization of a grain 1 The copper alloy by the process which controlled;, thus a series of manufacture conditions of performing 2 times solution treatment which made cold rolling intervening in the medium since Ti was fully dissolved to Cu Hardness, When it can have with sufficient balance on the high level expected many characteristics, such as conductivity, bendability, and a stress relaxation characteristic, as an object for the electrical and electric equipments of the present and future. By adding a proper quantity of Zn to Cu-Ti basic composition, and adding Cr, Fe, nickel, Sn and In, P, and/or Si as occasion demands further, the further betterment of soldering characteristics and a strength property also replaces it with possible; cold rolling, and Cold drawing, New knowledge that cold forging etc. is processible was able to be acquired.

[0009] This invention is completed by materializing the above-mentioned knowledge. Ti: 0.01 to 4.0% (% showing a component rate may be "weight %") is contained. Or [one or more sorts of Zn:0.05-2.0% and Cr, Zr, Fe, nickel, Sn and In, Mn and P and Si] further while containing 0.01 to 3.0% in a total amount The 1st solution treatment performed by the heat treatment condition to which less than 240 seconds and an average crystal grain diameter do not exceed 20 micrometers at the temperature beyond (1) 800 degree C to the copper alloy with which the remainder consists of Cu and an

unescapable impurity, (2) The 1st cold rolling performed with less than 80% of workability, the 2nd solution treatment performed by the heat treatment condition used as the range in which less than 240 seconds and an average crystal grain diameter do not exceed 1-20 micrometers at the temperature beyond (3) 800 degree C, (4) It is the method characterized by performing aging treatment of less than 15 hours one by one for 1 hour or more at the 2nd cold rolling performed with 50% or less of workability, and (5)300-700 degree C temperature.

[Function] The component composition of this invention and the Reason for definition of manufacture conditions are hereafter explained in full detail with the operation.

When aging treatment of the Cu-Ti alloy is carried out to Ti:Ti, spinodal decomposition is caused and the modulated structure of concentration is made in a base material, and it is this. Although there is an operation which secures very high hardness Since a desired consolidation cannot be expected at less than 0.01%, but it becomes easy to cause the deposit of a grain community reaction type which makes Ti contain exceeding 4.0% on the other hand, and strength reduction was caused conversely or the content deteriorated workability, the Ti content was determined as 0.01 to 4.0%.

[0011] Since Zn:Zn can expect the operation which improves solder heat resistance detachability without reducing the conductivity of a Cu-Ti alloy, Although added if needed, an effect operation of the request by the content being less than 0.05% was not obtained, but since conductivity and a stress relaxation characteristic deteriorated when it became the content exceeding 2.0% on the other hand, the content of Zn determined it as 0.05 to 2.0%.

[0012] Each of Cr, Zr, Fe.nickel, Sn and In, Mn, P and Si:Cr, Zr, Fe(s), and nickel does not reduce the conductivity of a Cu-Ti alloy greatly, controls a grain boundary type deposit, miniaturizes a crystal grain diameter and has an operation of raising hardness by aging deposit further. Moreover, Sn, In, Mn, P, and Si have the operation which raises the hardness of a Cu-Ti alloy mainly by solid solution strengthening. Therefore, if it becomes the content in which one sort or the desired effect according that the content is less than 0.01% in a total amount although added by two or more sorts to said operation is not acquired, but these elements exceed 3.0% in a total amount on the other hand as occasion demands, the conductivity of a Cu-Ti alloy and workability will be deteriorated remarkably. For this reason, the content of Cr, Zr, Fe and nickel with which one sort of independent addition or two or more sorts of compound addition are made, Sn and In, Mn, P, and/or Si determined it as 0.01 to 3.0% in the total amount.

[0013] Then, a manufacturing process is explained. In this invention, it has been to bases to perform the process of solution treatment and cold rolling following this twice, and to perform aging treatment after that. That is, since it is difficult to obtain a particle size regulation organization, securing hardness by the method of performing general solution treatment and cold rolling once, the characteristics of the Cu-Ti-(Zn) alloy are made into the above-mentioned process which can fully be demonstrated. The manufacture conditions which explain the Reason for definition below are also set up from such a viewpoint.

[0014] In solution treatment this invention, in order to obtain the ingredient of high intensity by next aging treatment by making Ti fully dissolve, the first time and the second solution treatment temperature are 800 degrees C or more. That is, in treatment temperature, at less than 800 degrees C, Ti is un-dissolving depending on the content of Ti, and the high intensity which is the feature of an age-hardening ingot copper alloy is not obtained. As for making it into less than 240 seconds, the ingredient retention time, i.e., "processing time", of 800 degrees C or more in temperature, big and rough-ization of a grain takes place by the processing time for 240 seconds or more. [0015] Moreover, between two solution treatment, in the 1st solution treatment, it is required to adjust solution treatment time within in 240 seconds corresponding to the amount of Ti of a raw material, the crystal grain diameter before solution treatment, etc. so that an average crystal grain diameter may be 20 micrometers or less. A crystal grain diameter is controlled by 1st solution treatment as mentioned above in order to obtain the crystal grain diameter of 20 micrometers or less in the state of a particle size regulation by the 2nd solution treatment. That is, if the average crystal grain diameter after the 1st solution treatment exceeds 20 micrometers, even if it makes solution treatment temperature low and shortens processing time noting that I will obtain the average crystal grain diameter of 20 micrometers or less by the 2nd solution treatment, a mixed grain size or a nonrecrystallized part will arise.

[0016] Moreover, the average crystal grain diameter after the 2nd solution treatment shall be 1-20 micrometers, in order that a grain may affect bendability and a stress relaxation characteristic greatly. When the average crystal grain diameter used such a microcrystal ingredient as a flat spring in less than 1 micrometer, a stress relaxation characteristic worsens and this is used as a flat spring, lowering of a spring pressure arises at an early stage. Moreover, when it exceeds 20 micrometers, it becomes easy to produce surface deterioration on the surface in the case of bending, and it may be divided when a bend radius is small. Although the cooling method in particular after solution treatment is not limited, it is desirable to carry out with air cooling or water cooling whose cooling rate is quick enough so that Ti may not deposit.

[0017] Since it becomes difficult for work hardening to advance the reduction of area of an ingot remarkably on real operation as the workability of cold rolling of the 1st cold rolling is 80% or more, 1st cold rolling is performed with less than 80% of arbitrary workability. However, 30% or more is desirable. Since development of the texture by rolling will arise notably, anisotropy will become large and the bendability in the bending shaft of a rolling direction and the right-angled direction will deteriorate if it carries out with the workability exceeding 50%, 2nd cold rolling is performed with 50% or less of workability.

[0018] Aging treatment aging treatment is performed at 300-700 degrees C in order to raise hardness and conductivity. Aging treatment temperature takes [aging treatment] time at less than 300 degrees C and is not economical, and since Ti will dissolve depending on a Ti content and the hardness and conductivity which are the feature of an age-hardening type alloy will not be acquired if it exceeds 700 degrees C on the other hand, the aging treatment of a 300-700-degree C temperature range is

required. When it is stabilized and hardness and conductivity are raised, the aging treatment in 420-480 degrees C is recommended in real operation. Since lowering of the hardness by remarkable overaging will take place if the hardness according [aging time] to aging and conductive improvement cannot be expected but it exceeds 15 hours, 1 to 15 aging hours are required in less than 1 hour.

[0020] In addition, in the manufacture method of this invention, unless the average crystal grain diameter and final-cold-rolling workability after solution treatment are very important in order to obtain good bendability, and the conditions which both the both specified are fulfilled, the ingredient which has good bendability is not obtained. Based on the specification of the board thickness defined for the specific application of a Cu-Ti alloy in real operation, or others, it is within the limits and they are [above-mentioned] workability, temperature, and time. Although naturally adjusted, incidentally tensile strength is about 980Ns/mm2. A spring threshold value is about 950Ns/mm2 above. Above, the above-mentioned conditions are adjusted so that 13% of more than the electrical conductivity IACS may be obtained.

[0021]

[Example] Then, the example which shows the desirable alloy composition range especially explains this invention still more concretely. First, electrolytic copper or oxygen free copper was used as the raw material, and the copper alloy ingot (20mm in thickness) of the various presentations shown in Table 1 (EXAMPLE) and 2 (comparative example) with a high frequency vacuum melting furnace was ingoted. Next, in order to adjust to each [these] ingot at the crystal grain diameter in front The 1st solution treatment (850 degree-Cx 0.0458 hour (165 seconds)), 40% of 1st cold rolling, 2nd solution treatment (850 degree-Cx 0.017 hour (60 seconds)), 2nd cold rolling, and aging treatment (430 degree-Cx 8 hours) were performed one by one, and it was considered as the 0.30mm plate. [0022] And various kinds of specimens were extracted from the plate obtained by the time of performing a series of above-mentioned treatment, material testing was done, and the characteristics as spring material were evaluated by investigating "hardness", "conductivity", "spring nature", "bendability", and a "stress relaxation characteristic." Among these characteristics, "hardness" and "elongation" were measured by the tension test, and "conductivity" measured electric conductivity (% IACS) and they searched for it. Moreover, the spring threshold value (Kb) was measured about "spring nature."

[0023] Next, about "bendability", bending was performed with the W-bending testing machine, and the grade of surface deterioration and the existence of the crack were investigated and evaluated by carrying out visual observation of the bending part. in addition, an evaluation result has no development of O:surface deterioration and a crack -- x:surface deterioration or a crack displayed by the development.

[0024] Moreover, while fixing one end of a strip specimen, after having carried out load of the stress to the other end, applying the bending stress and holding at 200 degrees C in this condition for 1000 hours, also when a stress was opened wide, the method of measuring distortion which remains in

addition estimated the "stress relaxation characteristic."

[0025] Furthermore, hold in 1000 hours to a 150-degree C elevated-temperature tub, and take out every 100 hours in the meantime, after performing solder (90%Sn-10% Pb) plating of 5-micrometer thickness to a raw material. With the approach of giving one 90-degree bending round trip, and investigating the time of onset of solder exfoliation, "solder heat resistance detachability" was investigated and what did not have exfoliation till 1000 hours displayed results of an investigation as "1000hr." These results of an investigation are shown in Table 3 (EXAMPLE) and 4 (comparative example).

[0026]

[Table 1]

Product made from a presentation ** ** At the time of affair solution treatment 2 Eye Time Aging Treatment TiZn in Addition to this -- Cu reaches. Crystal grain diameter cold rolling Time impurity (micrometer) 1st workability The 2nd time (%) (hr) 1 3.2-** 10204082 2.9 1.2 ** 1510458 3 2.9 - Sn0.17 ** 12.5 12.5 40 8 4 3.0 - P 0.21 ** 12.5 15 50 8 5 3.4- Notes 1 ** 1010508 6 3.1- Notes 2 ** 1510408 7 3.3- Notes 3 ** 1020508 8 2.9 1.7 Notes 4 ** 1012.5 408 9 3.1 0.6 Notes 5 ** 1515408 10 3.1 1.3 Notes 6 ** 2015408 11 2.9 1.4 Notes 7 ** 10 10 40 8 12 3.0 0.8 Note 8 ** 15 10 50 8 13 3.0 1.3 Notes 9 ** 1512.5 458 14 3.2 1.5 Notes 10 ** 1012.5 408 15 3.0 1.6 Mn0.42 ** 12.5 10408 16 2.9 0.8 In ** 1010458 17 2.9 1.2 Si ** 101045818 3.2 1.4 Fe ** 1012.5 408 19 2.9 1.0 Nickel ** 15 10 40 8 20 3.1 1.2 Cr ** 10 12.5 50 8 21 3.1 0.8 Zr ** 15 12.5 45 8 [0027] Notes 1: In 0.32, Si 0.07, Fe0.02 notes 2: Sn 0.24, Mn 0.15, and Cr 0.05, Zr0.08 and nickel0.01 notes 3: Cr 0.12, Zr 0.15, Fe 0.06, and nickel0.04 notes 4: In 0.30, Mn 0.14, and P0.13 notes 5: Sn 0.10, In 0.15, Si 0.12, and Fe0.13 notes 6: Sn 0.12, In 0.07, Mn 0.21, P0.08, Si0.13 notes 7:P0.06, Si 0.04, Cr 0.32, Zr 0.05, Fe 0.12, nickel0.14 notes 8:Sn 0.32, In 0.12, Mn 0.21, and P0.04, Si0.03 notes 9:Cr 0.28, Zr 0.12, Fe0.02 notes 10:Cr 0.43, Zr 0.04, Fe 0.21, nickel0.26 [0028]

[Table 2]

Product made from a presentation ** ** At the time of affair solution treatment 2 Eye Time Aging Treatment TiZn in Addition to this -- Cu reaches. Crystal grain diameter cold rolling Time impurity (micrometer) 1st workability The 2nd time (%) (hr) 22 0.008 -- ** 101540823 0.006 1.5 Notes 1 ** 1020408 24 6.8 - Note 2 ** 10 20 40 8 25 5.4 0.8 Note 3 ** 10 10 45826 2.9 3.7 Notes 4 ** 151040827 3.1 1.4 Notes 5 ** 40 Non-recrystallized part 28 with 458 2.9 1.3 Notes 6 ** 1570408 29 3.0 1.5 Notes 7 ** 12.5 10858 30 3.1 1.5 Notes 8 ** 1010 45 20 31 2.9 1.8 Note 9 ** 12.5 10 45 0.5 32 3.2 - - ** - ** Grain 408 33 3.2 - - ** 10 - 40 8 34 3.2 - - ** 10 10 0 [0029] Notes 1: Sn 0.17, In 0.18, P0.04, Si0.03 notes 2: Sn 0.14, P0.12, Cr 0.31, Zr 0.15, Fe0.08 notes 3:In 0.26, P0.02, Zr 0.11, nickel0.05 notes 4:Sn 0.22, P0.15, Fe 0.03, nickel0.06 notes 5:Mn 0.22, P0.03, Si 0.07, Zr 0.14, Fe 0.06, and nickel0.12 notes 6: Sn 0.15, In 0.07, Mn 0.06, Si 0.08, Fe0.14 notes 7:P0.08, Si 0.18, Cr 0.23, nickel0.07 notes 8:Sn 0.26, Mn 0.18, Cr 0.42, Zr0.II, and Fe0.01 notes 9: It is that an underline among In 0.21, Mn 0.03, Zr 0.08, Fe 0.14, and nickel0.I6 table is a value besides this invention. It means.

[0030]

[Table 3]

**** Spring electrical-and-electric-equipment music Stress relaxation Solder heat resistance gold ******* Threshold value conductivity ** Characteristics exfoliation time No. (N / mm2) (%) (N) /mm2 (%IACS) Sex (%) (hr) 1 99012.297413.20 4.7100 2 98213.896013.40 4.61000 3 99212.598013.40 5.1100 4 100412.3985 13.0 O 4.5 100 5 1015 13.5 997 13.8 O 4.7 100 6 1017 13.0101014.40 4.5100 7 101312.4100615.30 4.8100 8 102713.7101714.40 5.01000 9 102014.5100814.50 4.31000 10 101815.7100913.80 5.2800 11 102513.2101513.30 5.41000 12 1020 15.2 1010 13.6 O 4.5 1000 13 1010 12.8 1000 14.7 O 5.31000 14 102114.4101414.10 4.2900 15 101514.0101214.00 4.3800 16 102013.7100013.40 5.0800 17 102414.2100513.00 5.2800 18 101015.099714.20 5.21000 19 100514.7982 13.80 4.5 1000 20 1030 12.8 1010 13.6 O 4.3 900 21 1017 14 . 0 998 14.1 O 4.2 1000 [0031]

[Table 4]

***** Spring electrical-and-electric-equipment music Stress relaxation Solder heat resistance gold ******** Threshold value conductivity ** Characteristics exfoliation time No. (N / mm2) (%) (N) /mm2 (%IACS) Sex (%) (hr) 22 60322.458215.20 6.0100 23 62221.759515.40 6.21000 24 65220.863014.30 5.3100 25 63821.5604 14.6 O 5.5 900 26 1012 12.4 992 8.4 O 10.4 900 27 874 11.785013.8x 6.01000 28 95015.493313.7X 3.7900 29 10305.8101214.2X 4.81000 30 91216.790014.0O 4.71000 31 88017.186213.2O 4.51000 32 87716.584813.5X 4.2100 33 1105 1.2 1088 13.7 X 5.3 100 34 617 23.2 588 14.0 O 5.1 100 [0032] The following thing is clear from the result shown in Table 3 and 4. That is, both this invention alloys 1-21 are all excellent in hardness, bendability, and a stress relaxation characteristic, and assessment good enough is obtained also about other characteristics.

[0031] On the other hand, the comparison alloy 22 and 23 do not have an enough Ti content, and since the Ti content is over the ceiling value, hardness is inferior in the comparison alloy 24 and 25. Moreover, since the Zn content is over the ceiling value, conductivity and a stress relaxation characteristic are greatly inferior in the comparison alloy 26. Since the crystal grain diameter at the time of the 1st solution treatment is over the ceiling value, the comparison alloy 27 is the example which a crystal grain diameter did not build and put well at the time of the 2nd solution treatment. Since the crystal grain diameter at the time of the 2nd solution treatment is over the ceiling value, bendability is inferior in the comparison alloy 28. Since the workability of the 2nd cold rolling is over the ceiling value, bendability is inferior in the comparison alloy 29. Aging treatment time is over the maximum, and since the comparison alloy 31 does not have enough aging treatment time, hardness is inferior in the comparison alloy 30. The comparison alloy 32 is the example which did not perform 1st solution treatment, it serves as a mixed grain size at the time of the 2nd solution treatment, and hardness and bendability are inferior in it. The comparison alloy 33 is the example which did not perform 2nd solution treatment, work hardening is remarkable and bendability is inferior in it. The comparison alloy 34 is the example which cold-rolled only once, and hardness is inferior in it.

[0033]

[Effect of the Invention] By adopting the manufacture method of this invention, it becomes possible to obtain the high strength copper alloy which does not have inferiority in a Cu-Be alloy with good bending characteristics and stress relaxation characteristic, and industrially very useful effects -- it can contribute to the miniaturization of electrical and electric equipments and thinning greatly -- are brought about.

[Translation done.]